SCIENCE FOR GLASS PRODUCTION

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EFFECT OF NICKEL SULFIDE INCLUSIONS ON THE SPONTANEOUS FAILURE OF TOUGHENED GLASSES

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Studies have shown that when smaller NiS inclusions are present the "heat-soak" method of rejecting toughened glasses does not completely guarantee that these glasses cannot fail spontaneously while in use. It is posited that the reason why glasses fail spontaneously is not so much the polymorphism of NiS as high stresses around NiS inclusions and, in consequence, a limitation on the "life" time of glass in accordance with the kinetic theory of long-term strength.

Before showing the effect of defects in the form of NiS inclusions on the strength of glass, it is useful to recall that there are two fundamental concepts of the mechanism of glass failure—mechanical and kinetic. In the first concept, which Griffiths formulated and to which foreign scientists mainly adhere in their own studies, the following is considered. Surface microcracks of definite length are present in real glass; overstresses arise in the most dangerous microcracks under internal or external stresses, and this causes these cracks to grow and results in failure of the glass. The following equation describes the condition for crack propagation:

$$\sigma \geq \sigma_{cr} = \sqrt{\frac{c\alpha E}{L}},$$

where σ is the applied stress; σ_{cr} is the critical stress; c is a constant; α is the surface energy; E is the modulus of normal elasticity; and, L is the crack length.

It follows from this equation that the longer a crack, the lower the critical stress is and vice versa. The following method is used to evaluate the strength of glass in a lot in practice. Glass samples are taken (Fig. 1), and cracks with a definite length are created on them mechanically. Different stresses are applied to the samples and then the duration of crack growth up to complete splitting of the glass is determined. Curves of the Weibull distribution are constructed. These curves are used to determine the "life" time of some article or another when estimating the working stresses.

According to the kinetic concept, which S. N. Zhurkov formulated, failure is viewed not as an initially critical stress state in the glass but rather as being the result of a process where certain bonds break and this process propagates in the material in time. This happens under the action of thermal fluctuations or any external loads. When the most highly stressed bond breaks stresses are redistributed to other bonds, new stressed bonds are formed and they also break under thermal action, and so on. The concept of longevity under a load, i.e., the time during which the process just described occurs, from the moment when the stress is applied to the glass up to the moment the glass fails, is introduced.

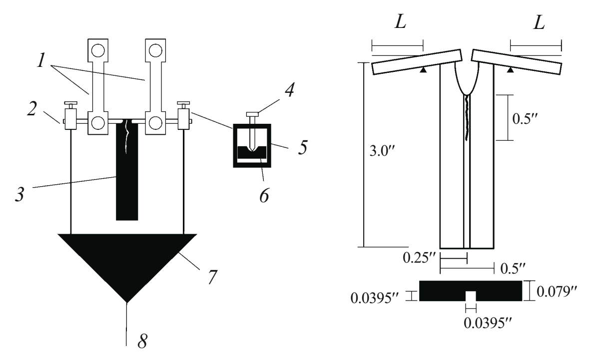

Fig. 1. Setup for evaluating the critical stresses in glasses: *1*) supporting arms; *2*) loading level; *3*) sample; *4*) screw; *5*) frame; *6*) loading levers; *7*) triangular bracket; *8*) load.

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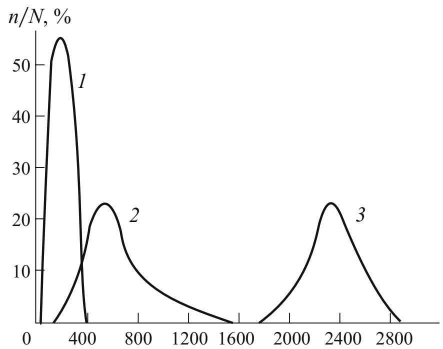

Fig. 2. Strength of chemically toughened glass: *1*) before chemical etching and without selection; *2*) same with selection; *3*) after chemical etching and selection.

Curves of the long-term strength of glass were established experimentally by a procedure developed at NITS OJSC. They are described by the equation

$$\log \tau = a - \gamma \log \sigma,$$

where τ is the "life" time of the glass up to failure; a and γ are constants; and, σ is the applied stress.

The constant a is determined by the relation

$$0 = a - \gamma \log \sigma_{\tau = 1} ,$$

where $a = \gamma \log \sigma_{\tau = 1}$ and is determined by the short-term strength of glass.

The long-term strength curves are constructed experimentally on the basis of tests performed on samples using the method of symmetric bending under instantaneous dynamic and different static loads. Curves of the long-term strength of glass are constructed on the basis of many such measurements.

The Russian scientists G. M. Bartenev, I. V. Razumovskii, A. I. Gubanov, A. D. Chevychalov, A. N. Orlov, V. I. Vladimirov, F. F. Vitman, V. P. Pukh, and others have made a large contribution to the development of the kinetic concept.

Investigations of the longevity of glasses and glass-based articles have been performed for more than 40 years and are successfully being continued at NITS OJSC. This work has confirmed the kinetic concept of the failure of glass as being more progressive. It is precisely the interpretation of this concept that enabled us to explain definitively the effect of surface and internal defects in glass on its strength.

It is customarily assumed that the large variance in the strength of silicate glasses is due to structural nonuniformities (microdefects) which are statically distributed throughout the volume of the glass.

There arise the obvious questions: what is the nature of these defects and can their distribution be controlled so as to bring the minimum strength values closer together?

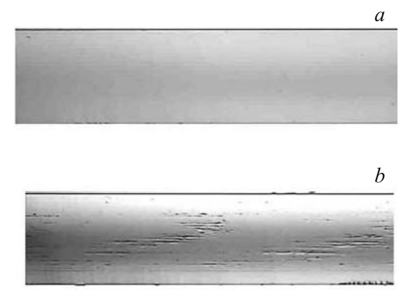

Fig. 3. Evaluation of defects by the laser splitting method: *a*) defect-free glass; *b*) glass with defects.

First, it is necessary to determine how the defects are distributed over the surface of a sample of sheet glass and how they influence the strength of the glass. This can be graphically demonstrated for glass before and after it is strengthened by chemical polishing. Clarifying this question would make it possible to determine which defects chemical polishing affects.

The strength distribution curves (V. P. Pukh's data) for the initial and chemically polished glass are displayed in Fig. 2. Measurements performed on a batch of samples which were visually inspected before and after etching for absence of defects show that eliminating defective samples (which comprise 10 – 20% of the number of samples) additionally increases the guaranteed minimum and average values of the glass strength.

Aside from the defects present on the surface of sheet glass, we also found internal defects which also affect the strength of glass. Macrodefects were found in glass while performing work in which a laser was used to split a sheet glass thermally. During the thermal splitting of sheet glass a through plane wave of tension stresses is created. This wave interacts with macrostresses or structural defects. This interaction introduces convex or concave formations of different form in the wave so that it is no longer plane. Figure 3 shows photographs of three-millimeter glasses after laser cutting. This method is very convenient for evaluating defects in glass: individual inclusions and cords, which cannot but affect the decrease of the strength of glass, are clearly visible.

The data presented on the presence of surface defects and defects in the interior volume of the glass prove once again that the mechanical concept, which ignores the presence of defects in the glass (aside from microcracks which are present initially), is not entirely correct for evaluating the strength parameters of real glass. The long-term strength of glass according to the kinetic concept depends on the presence of defects of some type or other, even if they are distributed statically and uniformly in the volume of the glass, and it is better grounded in our view.

We shall now examine the effect of NiS inclusions on the strength of toughened glass and evaluate the effect of such defects on the long-term strength on the basis of the kinetic concept of glass strength.

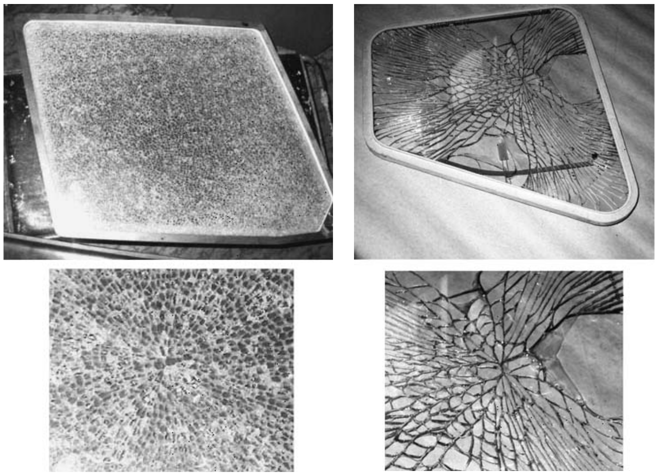

Fig. 4. Spontaneous failure of glass in a glass article.

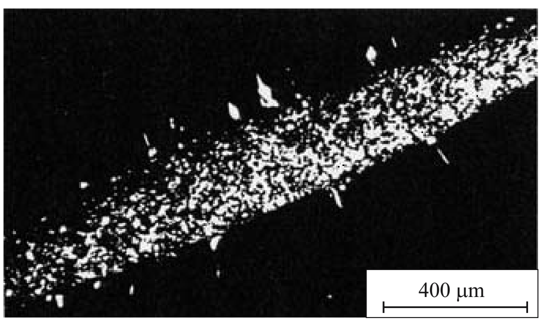

Fig. 5. Photomicrograph of a NiS crystal.

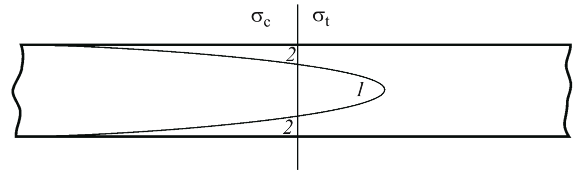

Fig. 6. Curve of the stress distribution in toughened glasses: *1*) zone of tension stresses σ_t ; *2*) zone of compression stresses σ_c .

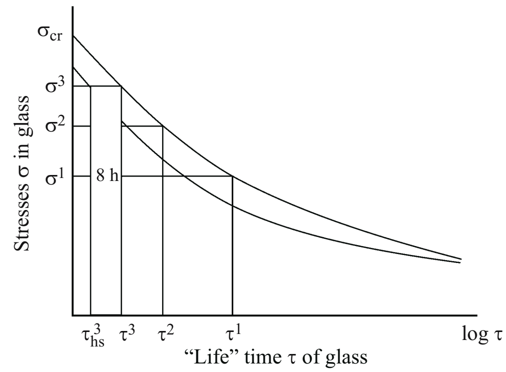

Fig. 7. "Life" time of glass versus stress due to different factors: σ^1, σ_{NiS}, and σ_{hs}) tension stresses due to toughening, NiS inclusions, and heating of glass according to the "heat-soak" method, respectively; $\sigma^2 = \sigma' + \sigma_{NiS}$; $\sigma^3 = \sigma' + \sigma_{NiS} + \sigma_{hs}$; τ^3 and τ^3_{hs} are the "life" times of glass before and after the "heat-soak" method is used.

A substantial number of articles concerning the phenomenon of spontaneous failure of silicate glasses have appeared recently in the foreign literature. In the works of Marger, Harris, Robert Lily, Tony Willmott, and other authors as well as some Russian specialists this phenomenon is linked to the presence of NiS inclusions in glass, which enter the glass with the batch during founding.

Foreign scientists explain spontaneous failure of toughened glass by changes in the volume of the NiS inclusions as a result of retarded transformation of NiS phases from a hexagonal high-temperature modification into a hexagonal rhombohedral low-temperature modification after the glass is thermally toughened.

Is this true?

We have also observed and studied spontaneous failure of the glass in multilayer articles as a result of the effect of NiS inclusions (Fig. 4). To explain the reasons for this phenomenon we applied the theory of the dependence of the long-term strength of glass on the actual total tension stresses present in the interior volume of glass as a result of various agents.

On the basis of radial microcracks which can be seen on the surface of a NiS crystal under a microscope (Fig. 5) the CLTE of the glass can be assumed to be higher than that of NiS, and this serves as a reason for the appearance of microcracks as glass cools during the manufacturing process. Therefore, substantial tension stresses are present in the zone of a NiS defect.

The presence of a NiS defect in glass is dangerous not only for the initial glass but also, and this is especially important, for toughened glass. A typical curve of the stress distribution over thickness in toughened glass is presented in Fig. 6. The appearance of a NiS defect in a tension stress zone causes such stresses to grow, which weakens the glass and sharply curtails its "life" time. The presence of such a defect in zone *2* is not so dangerous because compression stresses compensate the tension stresses due to NiS.

Practice and our own investigations have confirmed the aforesaid.

A typical curve of the long-term strength of glass is presented in Fig. 7. Evidently, the appearance of NiS in the tension stress zone in the glass during toughening increases total stresses cumulatively and sharply decreases the "life" time of the glass. If the glass failed during the toughening process, then this attests to the fact that the total stress exceeded the critical value.

Thus, spontaneous failure of glass as a result of the presence of NiS inclusions is most likely explained by a high level of the total stresses at the location of NiS and by a sharp decrease of the "life" time of the glass under the action of

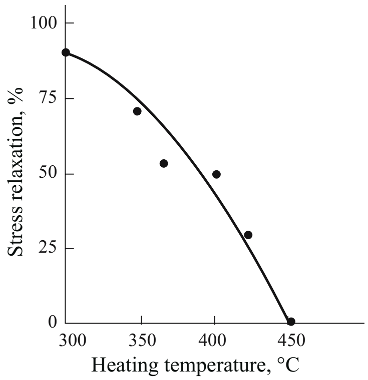

Fig. 8. Stress relaxation in toughened glass as a function of temperature with a soaking time of 1 h.

NiS and not by a change in the crystalline modification of NiS.

Everything would be fine if the problem of the effect of NiS were limited to scientific disputes. However, the mechanical concept has been used as the basis for developing standards and the “heat-soak” method. It is our opinion that the “heat-soak” method does not give a 100% guaranteed reason for rejecting toughened glasses, and in some cases it decreases the long-term strength of glasses which have not failed.

The essence of the “heat-soak” method consists in heating toughened glass to a temperature 250 – 300°C and holding the glass at this temperature for 8 h. There is no dispute that heating glass creates additional stresses, especially in the zone of a NiS defect, and if the critical stress in the process exceeds the strength of the glass, the glass will fail. But let’s examine the usefulness of the method from the standpoint of the kinetic concept.

Figure 8 shows a curve of the stress relaxation on heating toughened glass and soaking for 1 h. At 300°C the compression stresses evidently decrease in the toughened glass by approximately 10%. It is clear that for an 8-h soaking period these stresses be even lower as a result of relaxation. In this case soaking decreases the critical stresses on the curve of the long-term strength of the glass.

The results of an evaluation of the losses of glass longevity after prolonged heating up to temperature 250 – 350°C

TABLE 1.

Stresses in glass during use, MPa	Service longevity τ, h	
	for σ_{cr} = 100 MPa	for σ_{cr} = 70 MPa
30	4.4×10^{12}	7×10^{7}
40	5.8×10^{8}	1×10^{4}
50	5.5×10^{5}	10

with different working stresses in the glass are presented in Table 1.

It should be noted that the ultimate strength of toughened glass σ_{cr} = 100 MPa is of a static character and corresponds to an approximately 5% probability of failure, while after prolonged heating the ultimate strength of toughened glass is σ_{cr} = 70 MPa.

Studies performed by Dr. Harris and others of failures of toughened glass which are due to the NiS content show that the tension stresses around 50 ìm inclusions are 55 MPa. In this case he believes that this size is critical. As a result of “heat-soak” treatment we believe that smaller inclusions become dangerous for toughened glass.

In summary, long-time (several hours) testing of glass at high temperature decreases its service “life”, decreases σ_{cr}, and does not guarantee that the glass so tested will not spontaneously fail after the tests. In addition, the proposed rejection of glass on the basis of the “heat-soak” method is highly energy intensive, which affects the production costs.

Consequently, it would be useful to replace this method with a more progressive one. For example, high-resolution laser scanning for defects caused by NiS inclusions and other factors could be used. Glass can be put under controllable mechanical load for a short time, thereby creating additional tension stresses, or ultrasound can be used.

The American researcher J. E. Ritter writes: “Unfortunately, for purposes of predicting failure, data on the failure rate of cracks are not as reliable (mechanical concept — *present author*) as data obtained in experiments designed to determine the static or dynamic fatigue strength (kinetic concept — *present author*).” The interpretation of the effect of defects in the form of NiS inclusions on the process of spontaneous failure of toughened glasses proves his statement.